

TRANSPARENT GROUP III METAL NITRIDE AND METHOD OF MANUFACTURE

This application claims benefit under 35 U.S.C. §119(e) to U.S. Provisional Application No. 61/877,875, filed on Sep. 13, 2013; and this application is a continuation-in-part of U.S. application Ser. No. 14/089,281, filed on Nov. 25, 2013, which claims benefit under 35 U.S.C. §119(e) to U.S. Provisional Application No. 61/729,975, filed on Nov. 26, 2012; and this application is a continuation-in-part of U.S. application Ser. No. 13/894,220 filed on May 14, 2013, which is a continuation-in-part of U.S. application Ser. No. 12/634,665 filed on Dec. 9, 2009, which claims benefit under 35 U.S.C. §119(e) to U.S. Provisional Application No. 61/122,332, filed on Dec. 12, 2008; and this application is a continuation-in-part of U.S. application Ser. No. 13/041,199 filed on Mar. 4, 2011, which claims benefit under 35 U.S.C. §119(e) to U.S. Provisional Application No. 61/313,112, filed on Mar. 11, 2010; each of which is incorporated by reference in its entirety.

GOVERNMENT LICENSE RIGHTS

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FIELD

This disclosure relates to large-area, low-cost single crystal transparent gallium-containing nitride crystals useful as substrates for fabricating GaN devices for electronic and/or optoelectronic applications. The gallium-containing nitride crystals are formed by controlling impurity concentrations during ammonothermal growth and processing to control the types and relative concentrations of point defect species.

BACKGROUND

The present invention generally relates to processing of materials for growth of crystals. More particularly, the present invention provides a transparent gallium-containing nitride crystal synthesized by an ammonobasic or ammono-acidic technique. The present invention provides methods suitable for synthesis of polycrystalline nitride materials, as well as other crystals and materials. Such crystals and materials include, but are not limited to, GaN, AlN, InN, InGaN, AlGaIn, and AlInGaIn, and for manufacture of bulk or patterned substrates. Such bulk or patterned substrates can be used for a variety of applications including optoelectronic devices, lasers, light emitting diodes, solar cells, photoelectrochemical water splitting and hydrogen generation, photodetectors, integrated circuits, and transistors.

Gallium nitride containing crystalline materials serve as substrates for manufacture of conventional optoelectronic devices, such as blue light emitting diodes and lasers. Such optoelectronic devices have been commonly manufactured on sapphire or silicon carbide substrates that differ in composition from the deposited nitride layers. In the conventional Metal-Organic Chemical Vapor Deposition (MOCVD) method, deposition of GaN is performed from ammonia and organometallic compounds in the gas phase. Although successful, conventional growth rates achieved make it difficult to provide a bulk layer of GaN material.

Additionally, dislocation densities are also high and lead to poorer optoelectronic device performance.

Reasonably high quality, substantially transparent substrates comprising bulk gallium nitride are available commercially, however, in most cases, these substrates are synthesized by hydride vapor phase epitaxy (HVPE), which is relatively expensive.

What is needed is a method for low-cost manufacturing of transparent nitride materials that are transparent, colorless, and of high crystallographic quality.

SUMMARY

In a first aspect, a gallium-containing nitride crystals are disclosed, comprising: a top surface having a crystallographic orientation within about 5 degrees of a plane selected from a (0001)+c-plane and a (000-1)-c-plane; a substantially wurtzite structure; n-type electronic properties; an impurity concentration greater than about $2 \times 10^{17} \text{ cm}^{-3}$ of hydrogen; an impurity concentration less than about $1 \times 10^{17} \text{ cm}^{-3}$ of oxygen; an H/O ratio of at least 10; an impurity concentration greater than about $2 \times 10^{14} \text{ cm}^{-3}$ of at least one of Li, Na, K, Rb, Cs, Ca, F, and Cl; an optical absorption coefficient less than about 5 cm^{-1} at a wavelength of 400 nanometers; an optical absorption coefficient less than about 4 cm^{-1} at a wavelength of 410 nanometers; an optical absorption coefficient less than about 3 cm^{-1} at a wavelength of 415 nanometers; and an optical absorption coefficient less than about 2 cm^{-1} at a wavelength of 450 nanometers; wherein the gallium-containing nitride crystal is characterized by, an absorbance per unit thickness of at least 0.01 cm^{-1} at wavenumbers of 3218 cm^{-1} , 3202 cm^{-1} , and 3188 cm^{-1} ; and no infrared absorption peaks at wavenumbers between about 3175 cm^{-1} and about 3000 cm^{-1} having an absorbance per unit thickness greater than 10% of the absorbance per unit thickness at 3218 cm^{-1} .

In a second aspect, gallium-containing nitride crystals are provided, comprising: a top surface having a crystallographic orientation within about 5 degrees of a plane selected from a (0001)+c-plane and a (000-1)-c-plane; a substantially wurtzite structure; n-type electronic properties; an impurity concentration greater than about $5 \times 10^{17} \text{ cm}^{-3}$ of hydrogen; an impurity concentration between about $2 \times 10^{17} \text{ cm}^{-3}$ and about $4 \times 10^{18} \text{ cm}^{-3}$ of oxygen; an H/O ratio of at least 0.3; an impurity concentration greater than about $1 \times 10^{16} \text{ cm}^{-3}$ of at least one of Li, Na, K, Rb, Cs, Ca, F, and Cl; an optical absorption coefficient less than about 8 cm^{-1} at a wavelength of 400 nanometers; an optical absorption coefficient less than about 6 cm^{-1} at a wavelength of 410 nanometers; an optical absorption coefficient less than about 5.5 cm^{-1} at a wavelength of 415 nanometers; an optical absorption coefficient less than about 4 cm^{-1} at a wavelength of 450 nanometers; an absorbance per unit thickness of at least 0.01 cm^{-1} at wavenumbers of approximately 3175 cm^{-1} , 3164 cm^{-1} , and 3150 cm^{-1} ; no infrared absorption peaks at wavenumbers between about 3200 cm^{-1} and about 3400 cm^{-1} or between about 3075 cm^{-1} and about 3125 cm^{-1} having an absorbance per unit thickness greater than 10% of the absorbance per unit thickness at 3175 cm^{-1} .

In a third aspect, gallium-containing nitride crystals are provided, comprising: a top surface having a crystallographic orientation within about 5 degrees of a {1 0-1 0} m-plane; a substantially wurtzite structure; n-type electronic properties; an impurity concentration greater than about $3 \times 10^{18} \text{ cm}^{-3}$ of hydrogen; an impurity concentration between about $5 \times 10^{17} \text{ cm}^{-3}$ and about $3 \times 10^{19} \text{ cm}^{-3}$ of oxygen; an H/O ratio of at least 1.1; an impurity concen-